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RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

A REPORT TO

OFFICE OF NAVAL RESEARCH

AND

ADVANCED RESEARCH PROJECTS AGENCY

CONTRACT Nonr 2655(00)
ARPA ORDER NO. 170, AMENDMENT NO. 7
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FEBRUARY 1965

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CHEMICAL PRODUCTS DIVISION
AEROJET-GENERAL CORPORATION
AZUSA, CALIFORNIA

(0235)

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February 1965

Report No. 0235-01-21
(Quarterly)

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

By

K. Baum
V. Grakauskas
A. H. Remanick
O. S. Schaeffler

Analytical Support

C. L. Deuel
K. Inouye
H. Nelson

A Report To

OFFICE OF NAVAL RESEARCH
and
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Von Karman Center

AEROJET-GENERAL CORPORATION

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ABSTRACT

The reaction of α,α-dibromo-α-nitrotoluene with difluoramine and fuming sulfuric acid gave α,α-dibromo-α-difluoraminotoluene as well as α-bromo-α,α-bis(difluoramino)toluene. Attempts to apply more forcing conditions to this reaction resulted in explosions. No reaction occurred between bromopicrin and difluoramine in several attempts using different experimental conditions. α-Difluoramino-α,α-dichlorotoluene was prepared from α,α,α-trichlorotoluene and difluoramine.

α,α-Dibromo-α-difluoraminotoluene, α-bromo-α,α-bis(difluoramino)toluene and α-difluoramino-α,α-dichlorotoluene each reacted with methanolic sodium methoxide to give dimethyl carbonate anil.

Butyldifluoramine and sec-butyldifluoramine were obtained in 40-50% yields by the direct fluorination of n-butylurea and methyl sec-butylcarbamate, respectively, in acetonitrile solution. Direct fluorination of aqueous 3-hydroxypropylformamide gave 3-difluoraminopropyl formate. Some preliminary results on the fluorination of aldoximes are presented.

The preparation of fluoroammonium perchlorate was scaled-up to 2-3 g batches. The crude material was purified by crystallization from ethyl acetate-chloroform mixture.

CONTRACT FULFILLMENT STATEMENT

This is the twenty-first in a series of quarterly technical summary reports submitted in partial fulfillment of the contract. It covers the period 1 October through 31 December 1964.

AEROJET-GENERAL CORPORATION

E. M. Wilson

E. M. Wilson, Acting Manager
Chemical Products Division

CONTENTS

		Page
I.	INTRODUCTION	1
II.	TECHNICAL DISCUSSION	1
	A. Reactions of Difluoramine	1
	B. Direct Fluorination	7
	C. Fluorammonium Salts	11
III.	PERSONNEL	13

	Figure
Infrared Spectrum of α,α-Dibromo-α-difluoraminotoluene	1
Proton NMR Spectrum of α,α-Dibromo-α-difluoraminotoluene	2
Fluorine NMR Spectrum of α,α-Dibromo-α-difluoraminotoluene	3
Infrared Spectrum of α-Difluoramino-α,α-dichlorotoluene	4
Proton NMR Spectrum of α-Difluoramino-α,α-dichlorotoluene	5
Fluorine NMR Spectrum of α-Difluoramino-α,α-dichlorotoluene	6
Infrared Spectrum of sec-Butyldifluoramine	7
Proton NMR Spectrum of sec-Butyldifluoramine	8
Proton NMR Spectrum of Methyl N-Fluoro-N-sec-butylcarbamate	9
Fluorine NMR Spectrum of Methyl N-Fluoro-N-sec-butylcarbamate	10
Differential Thermal Analysis of Fluoroammonium Perchlorate	11

Distribution List

I. INTRODUCTION

The objective of this program is to develop new methods of preparing high-energy materials for military applications. During the period 1 October - 31 December 1964 covered in this report, research has continued on the reactions of difluoramine and on direct fluorination of nitrogenous compounds in solution. Increased effort has been directed toward the preparation and purification of larger amounts of fluoroammonium perchlorate. A discussion of the experimental results follows.

II. TECHNICAL DISCUSSION

A. REACTIONS OF DIFLUORAMINE (K. Baum)

1. Discussion

The reaction of α,α-dibromo-α-nitrotoluene with refluxing difluoramine in the presence of fuming sulfuric acid was previously shown to give α-bromo-α,α-bis(difluoramino)toluene.* This reaction was repeated under more stringent conditions, with the objective of replacing the remaining bromine atom. Several attempts were made to conduct the reaction at ambient temperature in a Teflon valve reactor, but explosions resulted each time.

The reaction at atmospheric pressure was repeated on a larger scale in order to obtain a quantity of α-bromo-α,α-bis(difluoramino)toluene sufficient for a study of its chemical properties. In addition to this compound, α,α-dibromo-α-difluoraminotoluene was also isolated:

$$C_6H_5CBr_2NO_2 \xrightarrow[H_2SO_4,\ SO_3]{HNF_2} C_6H_5CBr(NF_2)_2 + C_6H_5CBr_2NF_2$$

The infrared spectrum and the proton and fluorine NMR spectra of the latter compound are shown in Figures 1, 2, and 3, respectively.

*Aerojet-General Report 2945, October 1964, p. 3 (Confidential).

A similar reaction of bromopicrin with difluoramine would be expected to give tribromo(difluoramino)methane or subsequent bromine replacement products. When this reaction was conducted at atmospheric pressure, at the reflux temperature of difluoramine, for 4 hours, only the starting material was recovered:

$$Br_3CNO_2 \xrightarrow[H_2SO_4,\ SO_3]{HNF_2} \text{no reaction}$$

When the reaction was conducted at ambient temperature and autogenous pressure for 20 hours, again no reaction took place. It was thought that the unreactivity might be due to insolubility of bromopicrin in the reaction medium. Consequently, the reaction at atmospheric pressure was repeated, with the addition of enough nitromethane to give a homogeneous solution. Only nitromethane and bromopicrin were recovered. This technique was not attempted in a room temperature reaction because a mixture of fuming sulfuric acid and nitromethane was unstable under these conditions.

An unsuccessful attempt was also made to react difluoramine with the self-condensation product of nitroethane,* $CH_3-\underset{\underset{NO_2}{|}}{C}=N-OC(NO_2)_2CH_3$ or $CH_3-\overset{\overset{O}{\uparrow}}{\underset{\underset{NO_2}{|}}{C}}=N-C(NO_2)_2CH_3$. No reaction took place when fuming sulfuric acid and refluxing difluoramine were used. This unreactivity is surprising since one nitro group of this compound is readily replaced by HCl and alcohols.

The reaction of α,α,α-trichlorotoluene with refluxing difluoramine in fuming sulfuric acid gave α-difluoramino-α,α-dichlorotoluene in 65% yield:

$$C_6H_5CCl_3 \xrightarrow[H_2SO_4,\ SO_3]{HNF_2} C_6H_5CCl_2NF_2$$

The compound was characterized by elemental analysis, infrared (Figure 4), proton (Figure 5), and fluorine (Figure 6) NMR spectra.

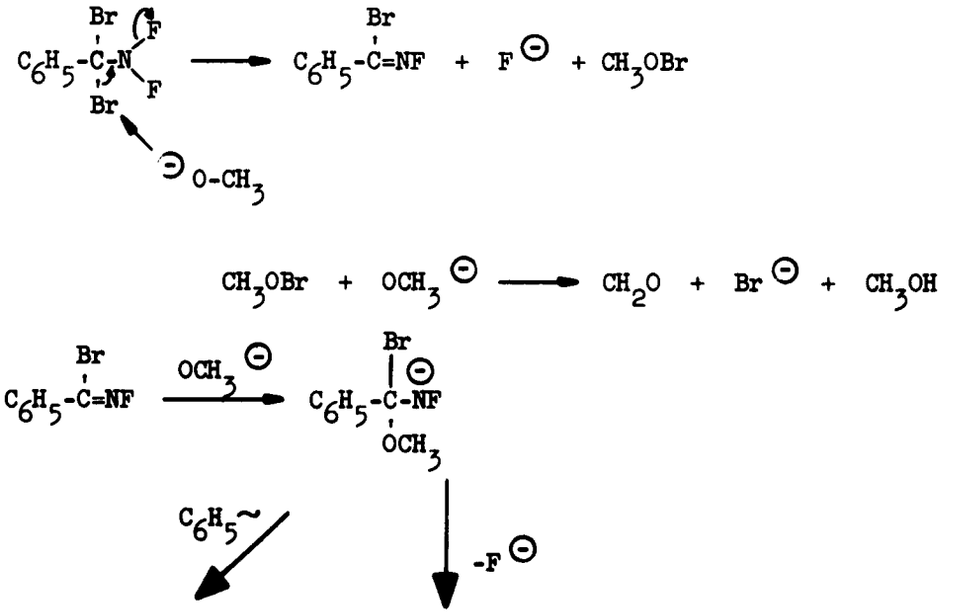
*J. S. Belew, C. E. Grabiel and L. B. Clapp, "Reaction of 1,1-Dinitroethane with Its Salts," J. Am. Chem. Soc., 77, 1110 (1955).

This compound and the above bromodifluoraminotoluene are convenient model compounds for a study of the chemical properties of α-halodifluoramines. The reactions of these compounds with methanolic sodium methoxide were studied to determine whether halogens adjacent to difluoramino groups can undergo displacement and whether the difluoramino groups are affected.

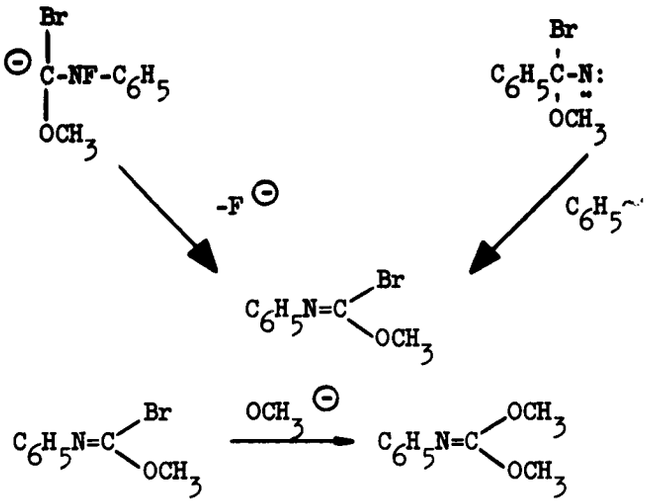
When α,α-dibromo-α-difluoraminotoluene was treated with methanolic sodium methoxide for 18 hours at room temperature, the product - isolated in 59% yield - was identified as dimethyl carbonate anil by means of elemental analysis, IR, and NMR spectra. The preparation of this compound was reported in 1892 by the reaction of phenyl isonitrile dichloride with sodium methoxide:*

$$C_6H_5N{=}CCl_2 \xrightarrow[CH_3OH]{NaOCH_3} C_6H_5N{=}C(OCH_3)_2$$

The overall reaction of α,α-dibromo-α-difluoraminotoluene with methoxide must include a reduction step, a phenyl migration, and a bromine displacement. The following mechanism rationalizes the product, but other sequences of the steps are equally logical:



*A. Smith, J. Am. Chem. Soc., 16, 392 (1892).



The reaction of α,α-dichloro-α-difluoraminotoluene with sodium methoxide was slower than that of the bromo compound, and required heating. Under conditions that gave conversion of only a fraction of the starting material, dimethyl carbonate anil was also formed. Another compound, not yet fully characterized, was present which appears to be methyl chloroformate anil, on the basis of its NMR spectrum:

$$C_6H_5CCl_2NF_2 \xrightarrow[CH_3OH]{NaOCH_3} C_6H_5N{=}C(OCH_3)_2 + C_6H_5N{=}\overset{\overset{Cl}{|}}{C}{-}OCH_3 \quad (?)$$

α-Bromo-α,α-bis(difluoramino)toluene also reacted with methanolic sodium methoxide to give dimethyl carbonate anil:

$$C_6H_5CBr(NF_2)_2 \xrightarrow[CH_3OH]{NaOCH_3} C_6H_5N{=}C(OCH_3)_2$$

In this case a small impurity with infrared absorption at 5.80 μ was also produced.

The course of these reactions and the structure of the intermediates will be investigated further. Useful synthesis intermediates could result from this work if the reactions can be extended to halotris(difluoramino)methanes.

2. Experimental

a. Reaction of α,α-Dibromo-α-nitrotoluene with Difluoramine

To a refluxing mixture of approximately 58 g of difluoramine and 36 ml of 20% fuming sulfuric acid, 15 g (0.0508 moles) of α,α-dibromo-α-nitrotoluene was added dropwise with stirring. After 4 hours, 100 ml of pentane was added and stirring was continued for 15 min. The lower layer was drained onto ice and extracted with methylene chloride. Removal of the methylene chloride left only a trace of material. The pentane layer was flushed with nitrogen to remove difluoramine, and was drained into a flask containing several grams of sodium sulfate. Distillation of the pentane, followed by vacuum distillation of the residue, gave three fractions: 5.52 g with b.p. 41-43°C/0.65 mm; 0.63 g with b.p. 43-57°C/0.35 mm; and 4.98 g with b.p. 53°C/0.25 mm. The first fraction was identified as α-bromo-α,α-bis(difluoramino)toluene by its infrared spectrum, which was identical to that previously reported.* The highest boiling compound was identified as α,α-dibromo-α-difluoraminotoluene.

Anal. Calcd for $C_7H_5Br_2NF_2$: C, 27.9; H, 1.66; N, 4.65; F, 12.62.

Found: C, 28.0; H, 1.63; N, 4.70; F, 12.80.

The infrared spectrum, and the proton and fluorine NMR spectra of this compound are shown in Figures 1, 2, and 3, respectively. Deuterochloroform was used as the solvent for NMR, and tetramethylsilane (TMS) and Freon-11 were the references. The infrared spectrum of the intermediate distillation fraction indicated a mixture of the two identified compounds.

b. α-Difluoramino-α,α-dichlorotoluene

α,α,α-Trichlorotoluene (15 g, 0.078 mole) was added dropwise, with stirring, over a 15-min period, to a refluxing mixture of approximately 40 g of difluoramine and 36 ml of 20% fuming sulfuric acid. The reaction mixture was stirred for 4 hours. Pentane (100 ml) was then added and stirring was continued for 15 min. The lower layer was then drained onto ice and was discarded. The pentane solution was allowed to warm to 10°C, under a rapid nitrogen stream to

*Aerojet-General Report No. 2945, October 1964, Figure 1 (Confidential).

remove difluoramine, and was drained into a beaker containing some sodium sulfate. The pentane layer was decanted and the solvent was removed by distillation. Vacuum distillation of the residue gave 10.55 g (0.050 moles, 64% yield) of α-difluoramino-α,α-dichlorotoluene, b.p. 38°C/0.4 mm.

Anal. Calcd for $C_7H_5Cl_2NF_2$: C, 39.6; H, 2.36; N, 6.60; F, 17.9.

Found: C, 39.6; H, 2.02; N, 6.64; F, 17.8.

The infrared spectrum, and the proton and fluorine NMR spectra are given in Figures 4, 5, and 6, respectively. Deuterochloroform was used as the NMR solvent; TMS and Freon-11 were the references.

The impact sensitivity of this material was >90 cm vs 26 cm for RDX. The DTA showed only an endotherm at 216°.

c. Reaction of α,α-Dibromo-α-difluoraminotoluene with Sodium Methoxide

A solution of 0.06 moles of sodium methoxide in 23 ml of methanol was added dropwise to a solution of 3.42 g (0.0114 moles) of α,α-dibromo-α-difluoraminotoluene. The mixture was allowed to stand at ambient temperature for 18 hours. The solvent was removed using a rotary evaporator, and 50 ml of methylene chloride was added. Precipitated salts were filtered off and the solvent was again removed. Another 30 ml of methylene chloride was added and the solution was filtered and distilled. The residue was vacuum distilled to give 1.11 g (0.0067 moles, 59% yield) of dimethyl carbonate anil, b.p. 54-55°C/0.15 mm.

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.5; H, 6.66; N, 8.5.

Found: C, 64.8; H, 6.54; N, 8.22.

Gas chromatography (1/4-in. long by 10-ft column of 10% SE-30 silicone on Teflon at 145°C) showed two lower boiling impurities comprising 1.8% of the material. A sample of the major peaks was trapped for analysis.

Anal. Found: C, 65.3; H, 6.73; N, 8.5.

The infrared spectrum of dimethyl carbonate anil contains peaks at 3.30 μ (m), 3.36 (m), 3.50 (m), 5.97 (v.s.), 6.26 (s), 6.70 (m), 6.82 (s), 7.0 (s), 7.73 (s), 7.80 (s), 8.40 (s), 9.30 (s), 9.70 (s), 11.1,

12.6 (m), 13.3 (s), 13.9 (s), 14.35 (s), 15.3 (s). The proton NMR spectrum ($CDCl_3$ solvent, TMS reference) consists of a methoxy signal at 3.78 ppm and an aromatic multiplet centered at 421 cps.

d. Reaction of α-Bromo-α,α-bis(difluoramino)toluene with Sodium Methoxide

A solution of 0.025 mole of sodium methoxide in 10 ml of methanol was added dropwise, over a 15 min period, to 1.47 g (0.005 mole) of α-bromo-α,α-bis(difluoramino)toluene with 30 ml of methanol. The solution was allowed to stand at ambient temperature for 1 hour. The methanol was removed by means of an aspirator, and 30 ml of methylene chloride was added. The solution was filtered, stripped of solvent, and again diluted with 30 ml of methylene chloride, filtered, and stripped of solvent. The residue, 0.58 g, was shown to be mainly dimethyl carbonate anil by its infrared spectrum. There was a small extraneous peak, however, at 5.80 μ.

B. DIRECT FLUORINATION (V. Grakauskas)

1. Discussion

The fluorination of some simple nitrogenous compounds, which in aqueous solution gave low yields of the desired products, was reinvestigated in acetonitri- Thus, the fluorination of n-butylurea gave a mixture of n-$C_4H_9NF_2$, and n-C_4H_9NF ONF_2 from which n-butyldifluoramine was isolated in 50% yield. Similarly, the fluorination of methyl N-sec-butylcarbamate gave sec-$C_4H_9NF_2$ in 40% yield. The compound was identified by its infrared spectrum (Figure 7), its elemental analysis, and by its proton (Figure 8) NMR spectra. A small amount of N-fluoro derivative, sec-$C_4H_9NFCO_2CH_3$, was also isolated from the fluorination mixture and the compound identified by its NMR spectra (Figures 9 and 10). The preparation of sec-butyldifluoramine in general was similar to that of primary alkyldifluoramines, and it is likely that t-alkyldifluoramine could be also synthesized in the same manner.

The fluorination of N-3-hydroxypropylformamide in aqueous solution proceeded similarly to the reaction of a lower homologue* and gave 3-difluoraminopropyl formate, contaminated with some 3-difluoraminopropanol:

*Aerojet-General Report No. 2730 (Summary), October 1963, p. 25 (Confidential).

$$HCONH(CH_2)_3OH + F_2 \xrightarrow{(H_2O)} HCO_2(CH_2)_3NF_2 + NF_2(CH_2)_3OH$$

The ester was identified on the basis of its infrared spectrum and its elemental analysis.

3-Difluoraminopropanol was obtained in an acid-catalyzed transesterification of the ester with methanol. Its identification is not yet completed.

In a search for new classes of compounds that might react with fluorine to give NF derivatives, the fluorination of oximes was investigated. In aqueous solution, both n-butyraldoxime and acetaldoxime readily consumed fluorine, but the identification of reaction products in both cases was difficult. The crude fluorination mixtures were distilled over a wide range of temperature and underwent partial decomposition with the elimination of hydrogen fluoride. Therefore, only the corresponding nitriles (5-10% yield) could be positively identified among the reaction products. The ease of the fluorination, and the fact that nitriles were found among the reaction products, indicate that fluorination of oximes resulted in attack on either nitrogen or (less likely) on the -CH- portion of the molecule.

The above oximes were also fluorinated in the absence of a solvent at 0-5°C, and again fluorine was readily consumed. The same difficulties as described above were encountered in the isolation and identification of reaction products.

Finally, n-butyraldoxime and acetaldoxime were fluorinated in acetonitrile solution. In each case, the fluorination mixture was washed with a large volume of ice water at the end of the fluorination without apparent decomposition. The water-insoluble, liquid reaction products ($d > 1$) in each case weighed approximately as much as the starting materials. Attempts to purify these water-washed and dried reaction products, however, again led to partial decomposition and elimination of hydrogen fluoride.

The presence of water-insoluble reaction products in the acetaldoxime fluorination experiment definitely indicates that the material was neither acetonitrile, nor the starting material, because these two compounds are readily miscible with water. The crude fluorination mixture possessed very strong

oxidizing properties, implying the presence of NF bonding in the products. The NF compound, if present in the mixture at all, was relatively high boiling, because the bulk of the crude material boiled above 30°C at 0.2 mm pressure.

The fluorination of oximes is under further investigation.

2. Experimental

a. Fluorination of n-Butylurea

A solution (partial suspension) of 93 g (0.8 mole) of n-butylurea in 350 ml of acetonitrile was fluorinated at -10 to -20°C until approximately 1.6 moles of fluorine was consumed. Several localized fires occurred in the reactor at the beginning of fluorination, but the reaction proceeded smooth and fast as soon as all the starting material had dissolved.

A 50% aliquot of the fluorination mixture was concentrated at 20-25°C/25 mm to remove the mixture of the solvent, butyldifluoramine, and hydrogen fluoride. The distillate was washed first with 650 ml of ice water, followed by two more washings with 75 ml of cold water. The organic phase was separated, dried, filtered, and distilled to give 21 g (50% yield) of n-butyldifluoramine, identified by comparing its infrared spectrum with that of known material.

The distillation residue, after removal of n-butyldifluoramine, on further distillation gave ca. 12 g of material, b.p. 40-50°C/0.1 mm, which was dried, deacidified, and redistilled to give 10 g of a colorless liquid (b.p. 36-39°C/0.1 mm). This liquid was then tentatively identified as N-n-butyl-N',N'-difluorourea by comparing its infrared spectrum and its physical properties with those of analogous compounds.*

b. Fluorination of Methyl N-sec-Butylcarbamate

A solution of 66.5 g (0.5 mole) of methyl N-sec-butylcarbamate in 350 ml of acetonitrile was fluorinated at -20°C until approximately 1 mole of fluorine was consumed (3 hours). The fluorination mixture was washed first with 1000 ml, and then with three 70-ml portions of ice water; the crude material amounted to 35 g. The material was fractionated to give 25 g of sec-butyldifluoramine, b.p. 64-5°C, and 4.0 g of methyl N-fluoro-N-sec-butylcarbamate, b.p. 64-5°C/25 mm.

*Aerojet-General Report No. 0235-01-19 (Quarterly), April 1964, p. 15 (Confidential).

Anal. Calcd for $C_4H_9NF_2$: C, 44.03; H, 8.31; N, 12.83; F, 34.82.

Found: C, 43.6; H, 8.6; N, 13.0; F, 33.8.

The infrared spectrum of sec-butyldifluoramine is shown in Figure 7.

The 60-mc proton NMR spectrum (Figure 8) was obtained using a carbon tetrachloride solution with TMS added as an internal reference. The assignments are as follows. The slightly irregular triplet at 1.01 ppm is assigned to the CH_3CH_2- methyl group. The complicated multiplet with maximum intensity at 97 cps is assigned to $CH_3C\underline{H}_2$- methylene. The complex nature of this signal is attributable to the fact that the methylene group is attached to an asymmetric carbon $-CH_2\overset{*}{C}H(NF_2)CH_3$ and thus the methylene protons are non-equivalent. The doublet at 1.26 ppm is assigned to the $-CH(NF_2)C\underline{H}_3$ methyl group. The doublet components are further split by interaction with the $-NF_2$ fluorines. The broad, weak multiplet with maximum intensity at 200 cps is assigned to the $-CH_2C\underline{H}(NF_2)CH_3$ proton. If the fluorines are equivalent, the signal would be expected to take the form of a triplet of sextets. If, as seems more likely, the fluorines are non-equivalent, 24 lines would be expected. Thus, the complicated form of the signal is reasonable.

The 60-mc proton (Figure 9) and 56.4-mc fluorine (Figure 10) NMR spectra of $C_2H_5CH(CH_3)NFCO_2CH_3$ were obtained using a carbon tetrachloride solution with TMS and $CFCl_3$ added as internal references. The assignments are given below.

H'. The slightly irregular triplet at 0.97 ppm is assigned to the $C\underline{H}_3CH_2$- methyl group. The complex multiplet with maximum intensity at 101 cps is assigned to $CH_3C\underline{H}_2CH$-. The complicated nature of this signal is attributable to the asymmetric carbon atom to which this methylene group is attached. The doublet at 1.21 ppm is assigned to the $-CH(C\underline{H}_3)$- methyl group. The doublet components are further split by interaction with the NF fluorine. The intense singlet at 3.81 ppm is assigned to the carbomethoxy methyl $-CO_2C\underline{H}_3$. The pair (splitting 40.6 cps) of sextets at 3.95 ppm is assigned to the $-CH_2C\underline{H}(CH_3)NF$- proton. The high field sextet is overlapped by another weak signal or signals which are apparently due to an impurity.

F^{19}. The fluorine spectrum consists of a doublet (splitting 41.0 cps) at +97.51 ppm. The observed coupling is in good agreement with that obtained from the proton spectrum. A singlet of fairly high intensity is presumably due to an impurity.

c. Fluorination of 3-Hydroxypropylformamide

A solution of 77.5 g (0.75 mole) of 3-hydroxypropylformamide in 300 ml of water was fluorinated at 0-5°C until 1.5 moles of fluorine was consumed (4 hours). The fluorination mixture was extracted with three 75-ml portions of methylene chloride. The combined extracts were dried, deacidified with solid sodium bicarbonate, filtered, and concentrated. The residual material was distilled to give 38 g of a colorless liquid, b.p. 31-2°C at 0.1 mm. An analytical sample was purified by gas chromatography.

Anal. Calcd for $C_4H_7NF_2O_2$: C, 34.54; H, 5.07; N, 10.07; F, 27.3.

Found: C, 34.2; H, 5.4; N, 10.3; F, 29.1.

A portion of crude $HCO_2(CH_2)_3NF_2$ was transesterified with methanol (a drop of concentrated sulfuric acid used as the catalyst) by refluxing the solution for a period of 4 hours to give 3-difluoraminopropanol, b.p. 29-30°C/0.1 mm, n_D^{25} 1.3700. The characterization of this compound is not yet completed.

C. FLUOROAMMONIUM SALTS (A. H. Remanick and V. Grakauskas)

Some preliminary data on the purification of crude N-fluoroammonium perchlorate (SAP) by crystallization from ethyl acetate-chloroform mixture was presented in the previous report.* This crystallization procedure was pursued further during this quarter and SAP of 94-97% purity was obtained reproducibly; the material still contained 1 to 2% carbon. The NMR analysis of the crystallized SAP showed the presence of two impurities in approximately equal concentration. One of them, attributed to isopropylammonium perchlorate, was eliminated in subsequent batches of SAP by using higher purity isopropyl N-fluorocarbamate for the preparation of the crude material. The use of this high-purity starting material also resulted in a decrease of carbon content in crystallized SAP to

*Aerojet-General Report No. 2945 (Summary), October 1964, p. 37 (Confidential).

0.5-1.5%, representing only one contaminant as determined by NMR. This carbonaceous impurity was tentatively identified as isopropylidineimmonium perchlorate, and a possible route to its formation as a side reaction product in the hydrolysis step is visualized as follows:

$$NHFCO_2C_3H_7 + HClO_4 \longrightarrow NH_3F^{\oplus}ClO_4^{\ominus} + CO_2 + \left[C_3H_7^{\oplus}\right]$$

$$\left[C_3H_7^{\oplus}\right] + NHFCO_2C_3H_7 \longrightarrow C_3H_7NFCO_2C_3H_7 + H^{\oplus}$$

$$C_3H_7NFCO_2C_3H_7 + HClO_4 \longrightarrow C_3H_7NH_2F^{\oplus}ClO_4^{\ominus}$$

$$(CH_3)_2CHNH_2F^{\oplus}ClO_4^{\ominus} \longrightarrow (CH_3)_2C{=}NH_2^{\oplus}ClO_4^{\ominus} + HF$$

The immonium salt contaminant was probably present in all previous batches, but being less volatile the material remained as the sublimation residue during purification of crude SAP. This was found to be the case when crystallized SAP containing 1.2% of carbon was further purified by sublimation; the sublimed material was analytically pure. In this connection it was also found that crystallized SAP can be sublimed at a relatively fast rate without noticeable decomposition at 65°C. This purification technique will be applied to larger batches of crude material without prior purification by crystallization.

The preparation of SAP was scaled up to 2-3 g batches and no difficulties are anticipated in further scaleups. The larger amounts of the material now available will be used for storability tests and to study recrystallization techniques in an attempt to eliminate the carbonaceous contaminant.

The preliminary storability tests indicated that SAP containing 1 to 1.5% carbon decomposes gradually over a period of 4-7 days on storage at 25°C in either glass or Teflon containers. At sub-zero temperatures, the material is storable for at least several weeks without detectable change in its elemental analysis. It is possible that decomposition is catalyzed by the impurity and for comparison, the storability of sublimed SAP is now under investigation.

The DTA analysis (Figure 11) of sublimed SAP showed a main exotherm at 105°C; other less pronounced exotherm peaks at higher temperatures may result from the decomposition products - possibly $NH_4^{\oplus}$ or $N_2H_5^{\oplus}$ salts.

III. PERSONNEL

The experimental work was performed by K. Baum, V. Grakauskas, M. P. Mascari, A. H. Remanick, and O. S. Schaeffler. Analytical support was provided by C. L. Deuel (gas chromatograph), K. Inouye (microanalyses), and H. Nelson (IR and NMR).

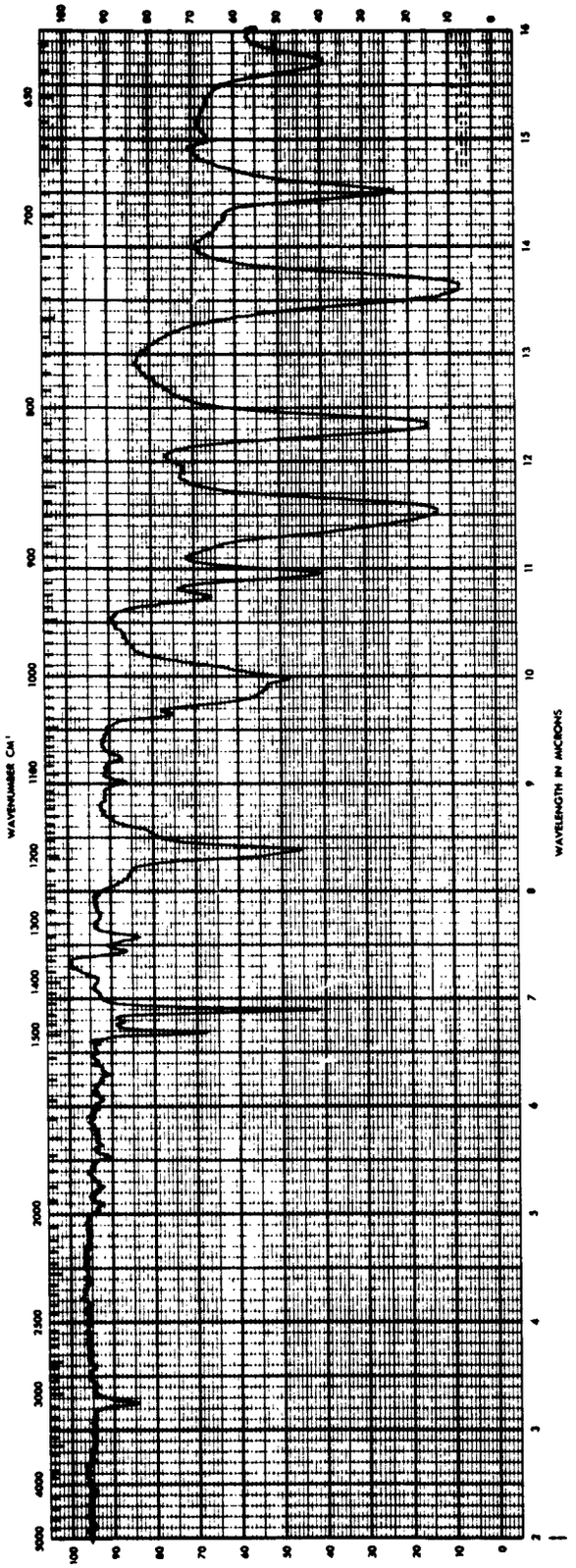


Fig. 1. Infrared Spectrum of α,α-Dibromo-α-difluoraminotoluene

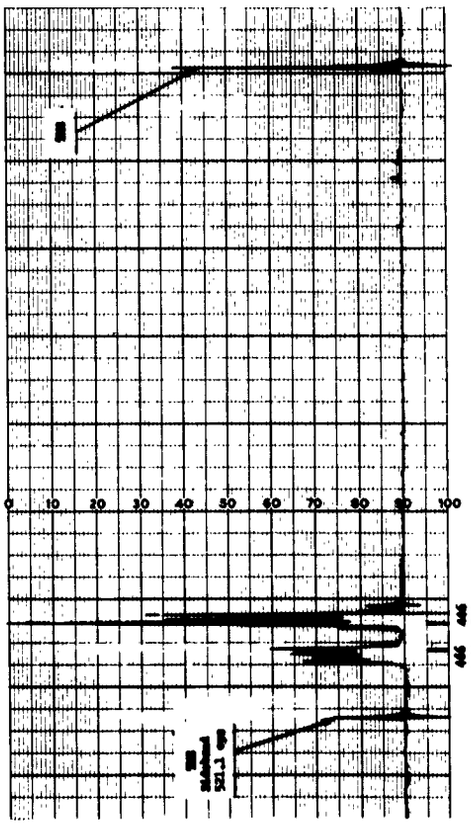


Fig. 2. Proton NMR Spectrum of α,α-Dibromo-α-difluoraminotoluene

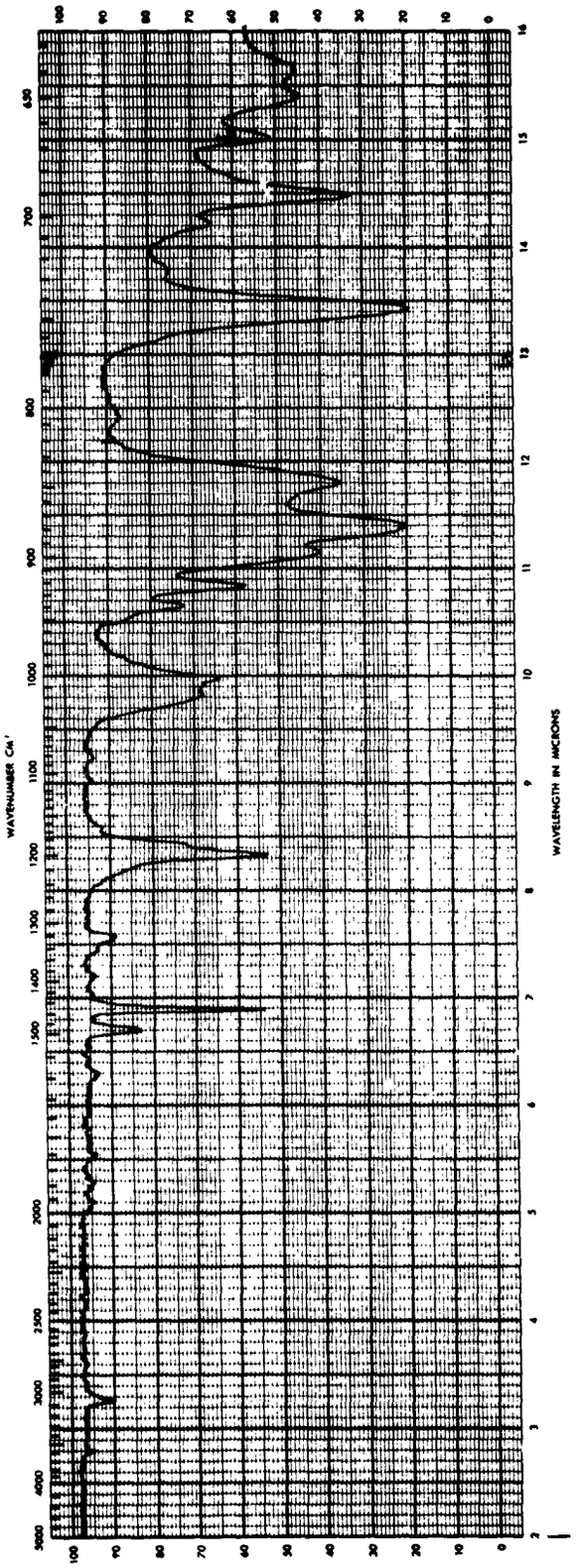


Fig. 3. Fluorine Spectrum of α,α-Dibromo-α-difluoraminotoluene

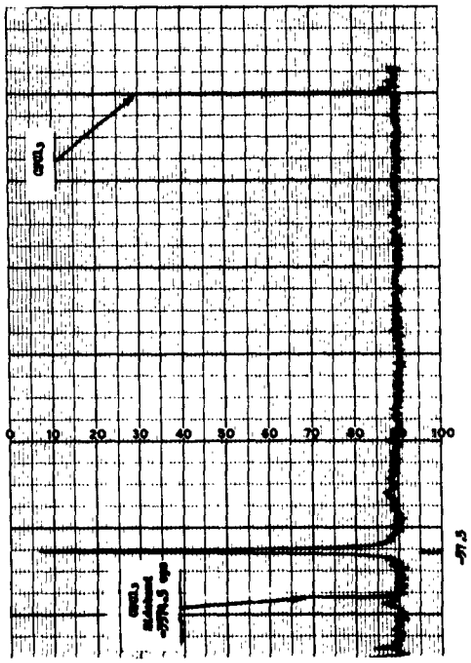


Fig. 4. Infrared Spectrum of α-Difluoramino-α,α-dichlorotoluene

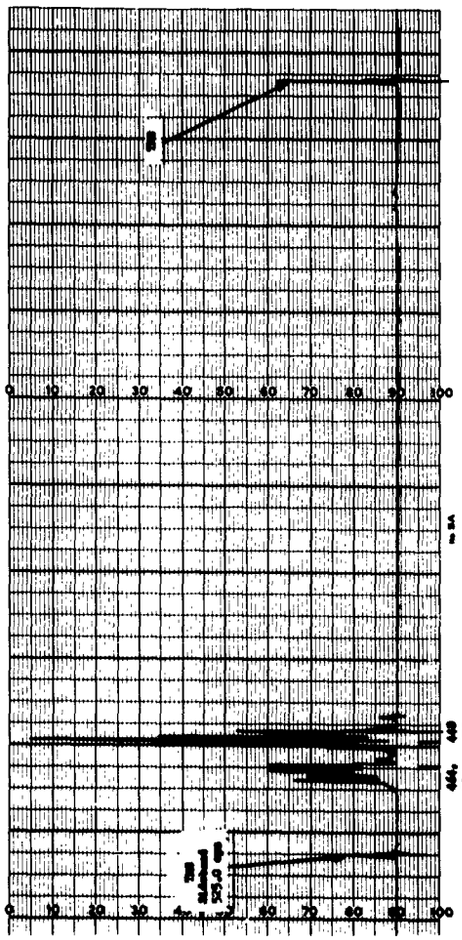


Fig. 5. Proton NMR Spectrum of α-Difluoramino-α,α-dichlorotoluene

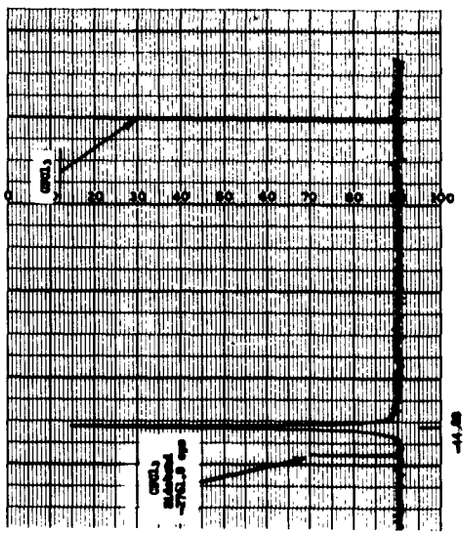


Fig. 6. Fluorine Spectrum of α-Difluoramino-α,α-dichlorotoluene

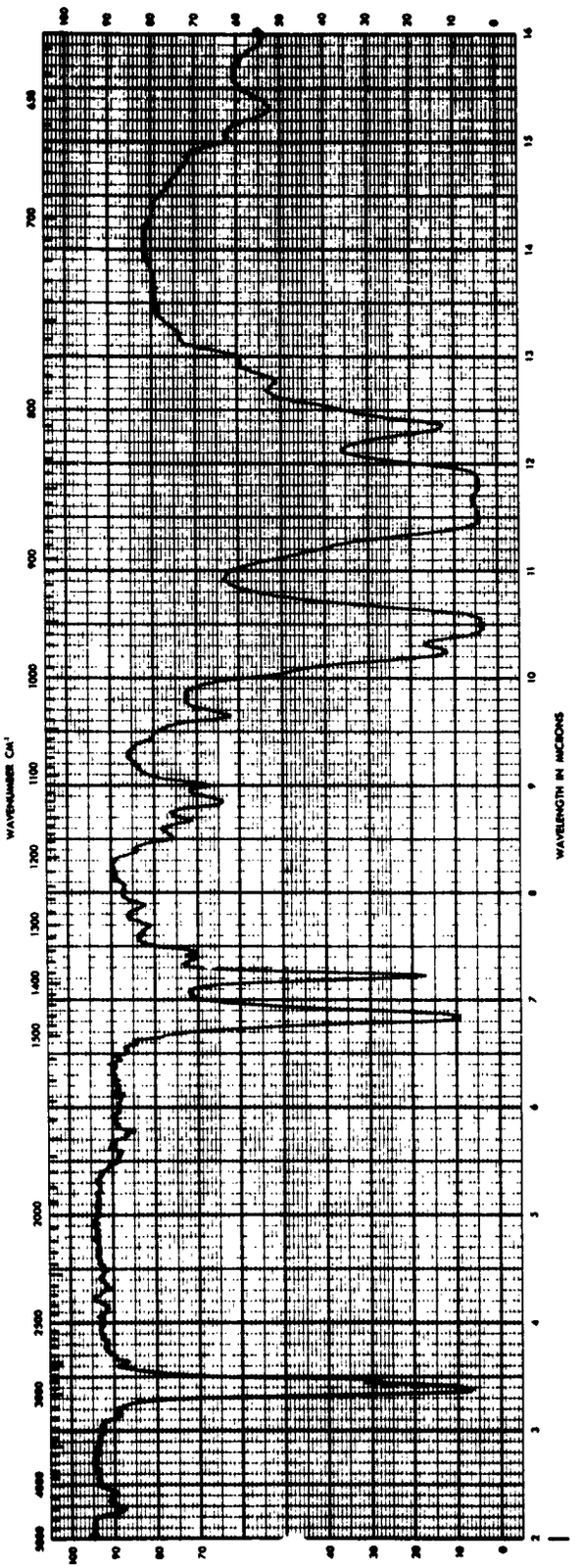


Fig. 7. Infrared Spectrum of sec-Butyldifluoramine

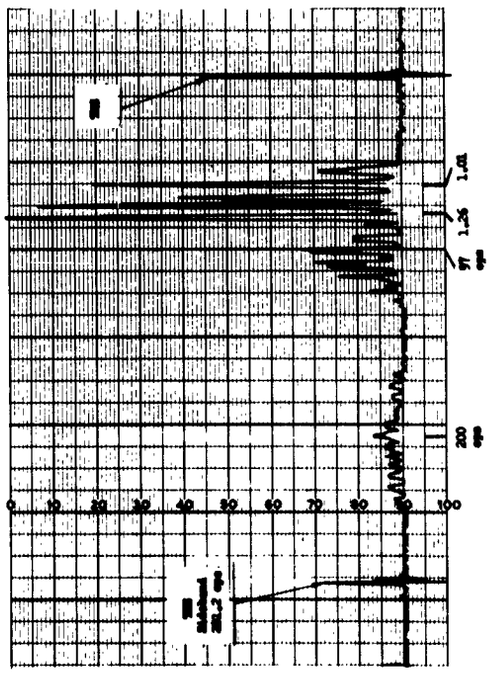


Fig. 8. Proton NMR Spectrum of sec-Butyldifluoramine

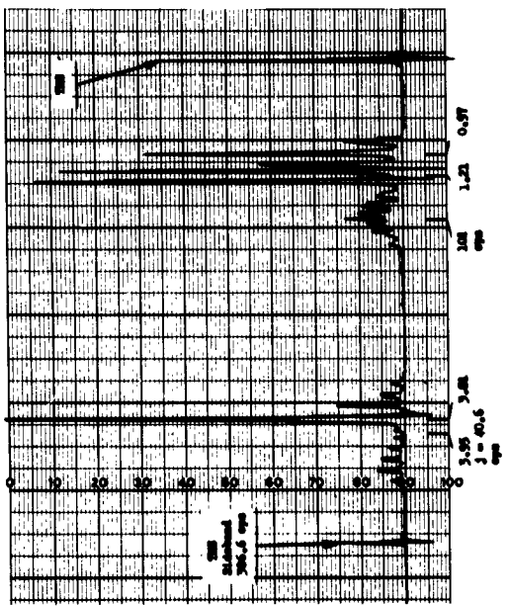


Fig. 9. Proton NMR Spectrum of Methyl N-Fluoro-N-sec-butylcarbamate

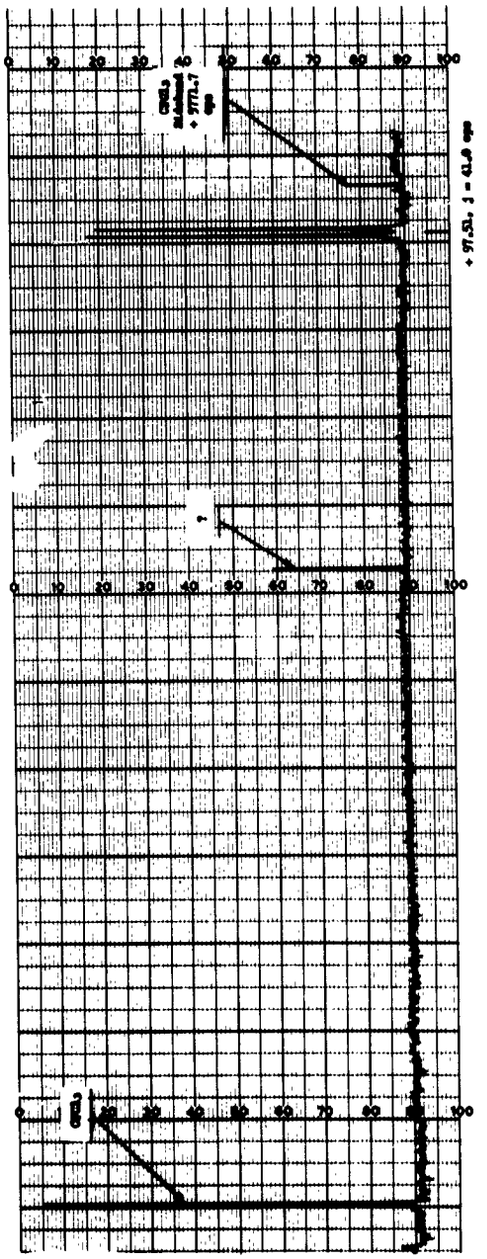


Fig. 10. Fluorine NMR Spectrum of Methyl N-Fluoro-N-sec-butylcarbamate

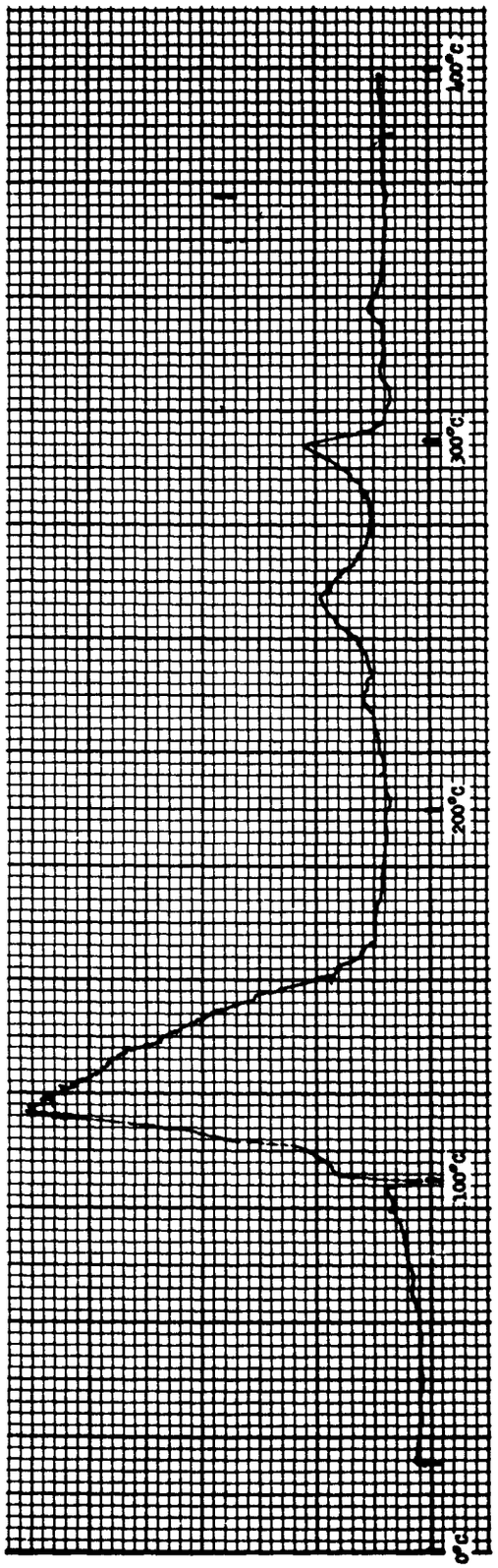


Fig. 11. Differential Thermal Analysis of Fluoroammonium Perchlorate

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